Materials from renewable resources based on furan monomers and furan chemistry: work in progress†

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The polymerisation of furan monomers and the exploitation of some of the chemical peculiarities of the furan heterocycle have generated a wide diversity of macromolecular materials based on renewable resources. We present here recent contributions to this field, including ongoing studies on the synthesis and characterisation of novel furan polyesters and on the application of the Diels–Alder reaction to the preparation of linear and branched thermally reversible polyadducts.

1. Introduction

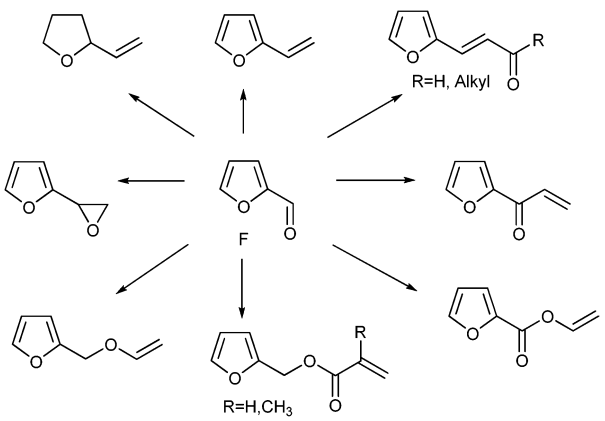
Making polymers from renewable resources is an old practice, as old as the birth of macromolecular science and technology toward the end of the nineteenth century. It was then that cellulose esters became important materials and the vulcanization of natural rubber brought tyres into the market. Together with these chemical modifications of natural polymers, "resins" based on terpenes, rosin and, later, furfuryl alcohol and alkyd compositions incorporating vegetable oils acquired growing applications.

The advent of the carbon, natural gas, and petroleum chemical revolutions in the twentieth century provided a myriad of novel macromolecular materials and thus fossil resources became the dominant precursors in this realm, with only modest additional original contributions from their renewable counterparts.

Nearing the end of the last century, the dwindling of fossil resources, together with their unpredictable price fluctuations, raised serious questions about the medium-term pursuit of their exploitation. This refers principally to energy production, but also to their becoming dominant purveyors of organic commodities and materials, with the additional concern of the ecological impact related to their exploitation. The ensuing surge of activities associated with the search for alternative energy sources has been extended to similar initiatives in the context of polymers from renewable resources, as recently reviewed.[1,2] Monomers, oligomers and polymers produced by nature within the multifarious biological activities associated with the animal and vegetable realms have thus regained a respectable status through the incessantly growing research aimed at turning them into useful materials. These investigations concern chemical transformations (polymerisation, surface or bulk modification, grafting and cross-linking) and/or physical manipulations (making blends, composites, and other multimaterials).

Among this burgeoning ferment of initiatives, polymers prepared from furan monomers and/or some specific features associated with the chemical peculiarities of that heterocycle constitute a unique class of materials based on vegetable renewable resources, because they encompass a wide variety of structures, simulating virtually all the current fossil-derived counterparts (furan itself was used as a precursor to polytetramethylene glycol, prior to its reduction to tetrahydrofuran).[2,3] This situation arises from the fact that two first-generation furan compounds, viz. furfural (**F**) and 5-hydroxymethylfurfural (**HMF**), readily prepared from polysaccharides or sugars bearing respectively pentose and hexose moieties, can be converted into two large families of monomers. The first refers to moieties susceptible to polymerise or copolymerise *via* chain-growth processes and includes structures derived from **F** by appending various vinyl moieties and acrylic or oxirane groups to the heterocycle, a selection of which is shown in Scheme 1, while the second concerns molecules for step-growth mechanisms, viz. monomers arising from **HMF** *via* the introduction, among others, of carboxy, hydroxyl, amino, or isocyanate functions, many of which are portrayed in Scheme 2. **HMF** is not sufficiently stable to be stored and recent production strategies envisage its in situ oxidation to the corresponding dialdehyde or diacid, both quite stable crystalline compounds.

In addition, difuran monomers for step-growth polymerisations can also be prepared using **F** derivatives and appropriate C5–C5 coupling reactions as sketched in Scheme 3.



Scheme 1 A selection of monomers derived from furfural (**F**).

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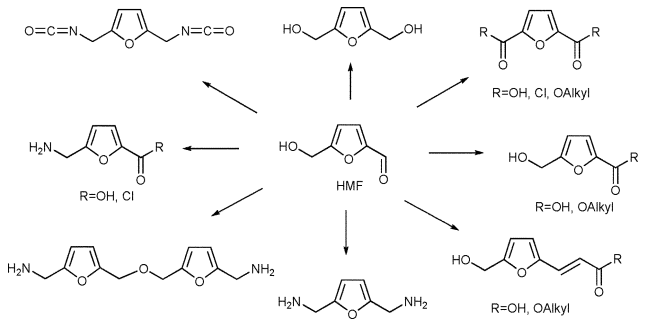
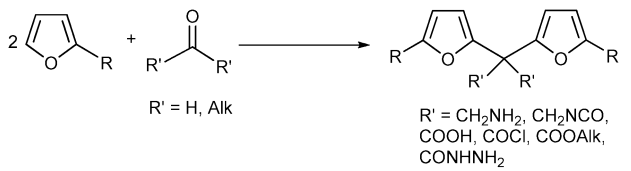


Scheme 2 A selection of monomers derived from 5-hydroxymethylfurfural (**HMF**).



Scheme 3 Difuran monomers derived from 2-substituted furans.

It is important to emphasise that all these monomers have already been synthesised and used in appropriate polymerisation and copolymerisation processes, followed by the characterisation of the ensuing materials.[2,3] This general strategy has therefore given rise to a novel realm of sustainable macromolecular science, which offers numerous promising alternatives to the corresponding conventional materials obtained from non-renewable sources. Clearly, the only originality of the structures shown in Schemes 1–3, and hence of the corresponding macromolecules, lies in their incorporation of the furan heterocycle, while otherwise simulating their classical aliphatic and aromatic counterparts. This is however a very important structural difference in terms of the unique possibility of making use of the heterocycle as a promoter of further polymer modifications thanks to its specific reactivity.

The exploitation of these peculiar chemical properties of the furan ring include, among others, (i) electrophilic substitutions to generate reactive end groups, block and graft copolymers, (ii) the coupling of photosensitive chromophores, (iii) the synthesis of conjugated molecules as powerful radical scavengers, and, principally (iv) its proneness to intervene in the Diels–Alder (DA) reaction, a beautiful example of reversible click chemistry, which has opened new ways to synthesise polymers with unique properties, including self-mendability and network recyclability through reversible cross-linking.[2–4]

Given that the outcome of all these studies has been largely documented, including a critical appraisal of the merits and drawbacks of each system in terms of monomer reactivity, side reactions and polymer properties,[2–4] the present report is restricted to our recent contributions to the field of furan-based polyesters and DA polymers, some of which are still in progress.

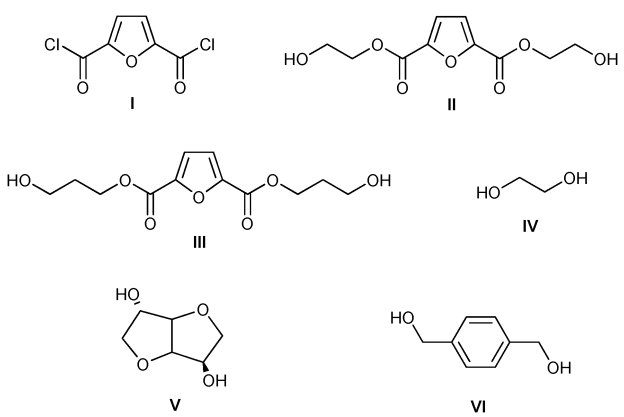
2. Experimental

This section only describes the synthesis and characterisation of the monomers used in both types of polymerisations, whereas the specificities associated with these different processes will be provided together with the actual results.

2.1 Monomers for polyesters

The pure 2,5-furandicarboxylic acid (**FDCA**) used in this study was a generous gift from Prof. Antoine Gaset of Toulouse National Polytechnic Institute.[5] Its purity, deemed adequate for its subsequent use as a precursor of the various monomers described below, was confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Its dichloride (monomer **I**, Scheme 4) was prepared by its reaction with an excess of thionyl chloride under reflux for 4 h, in the presence of DMF and purified by vacuum sublimation to give white crystals (78% yield), m.p. 79 °C. ν (FTIR-ATR)/cm^{-1} 3140 and 3110 (furan C=C), 1737 (C=O) and the typical peaks of ring breathing (1007) and of 2,5-substituted furans (824 and 712); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.54 (2H, singlet, furan H3 and H4); δ_C (75 MHz, $CDCl_3$, Me_4Si) 123.2 (furan C3 and C4), 149.3 (furan C2 and C5) and 155.9 (C=O). The sensitivity of **I** to hydrolysis was found to be quite modest, as shown, on the one hand, by its stability in ambient conditions for several days and, on the other, by the fact that when suspended in water at room temperature, its FTIR spectrum only began to show the formation of the corresponding acid after about 30 min.

Bis(hydroxyethyl)-2,5-furandicarboxylate (monomer **II**, Scheme 4) was obtained in 98% yield by the HCl-catalysed esterification of **FDCA** with a large excess of ethylene glycol, followed by its purification by high-vacuum distillation of the excess glycol: ν (FTIR-ATR)/cm^{-1} 3340 (OH), 1716 (C=O), 1020 (ring breathing) and 887 + 771 (2,5-dibustituted furan); δ_H (300 MHz, C_3D_6O, Me_4Si) 3.86 (4H, triplet, CH_2OH), 4.38 (4H, triplet, COOCH_2), 7.37 (2H, singlet, furan H3 and H4) and a broad O*H* peak between 3.5 and 4.2; δ_C (75 MHz, C_3D_6O, Me_4Si) 60.6 (*C*H_2OH), 67.6 (COO*C*H_2), 119.7 (furan C3 and C4), 147.7 (furan C2 and C5) and 158.7 (C=O). A similar procedure was adopted to prepare and purify bis(hydroxypropyl)-2,5-furandicarboxylate (monomer **III**, Scheme 4) using 1,3-propylene glycol. Its FTIR spectrum was, as expected, very similar to that of **II**. In its ^{1}H and ^{13}C NMR spectra, the only relevant difference with respect to those of **II** was the extra peak at 2.0 ppm for the intermediate CH_2 protons and at 33.9 ppm for



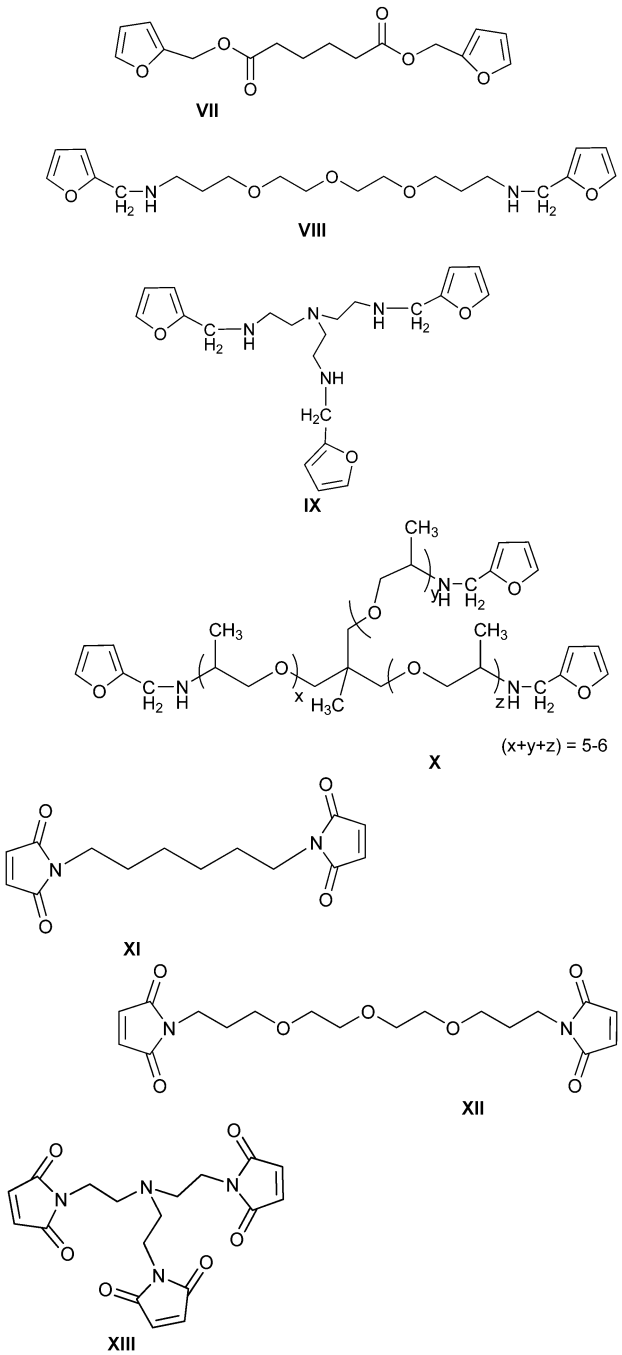
Scheme 4 Monomers used to prepare furan-based polyesters.

its carbon atom. ν (FTIR-ATR)/cm^{-1} 3279 (OH), 3152 + 3120 (furan C=C), 2966 + 2928 + 2872 (CH_2), 1725 (C=O), 1023 (ring breathing) and 885 + 770 (2,5-dibustituted furan); δ_H (300 MHz, $CDCl_3$, Me_4Si) 2.00 (4H, quintet, $CH_2CH_2CH_2OH$), 3.78 (4H, triplet, $CH_2CH_2CH_2OH$), 4.50 (4H, triplet, $COOCH_2$),7.22 (2H, singlet, furan H3 and H4) and a O*H* peak at 2.19; δ_C (75 MHz, $CDCl_3$, Me_4Si) 33.9 ($CH_2CH_2CH_2OH$), 58.9 ($CH_2CH_2CH_2OH$), 62.6 ($COOCH_2$), 118.6 (furan C3 and C4), 146.6 (furan C2 and C5) and 158.2 (C=O). Ethylene glycol (monomer **IV**, Scheme 4) of the highest purity commercially available was used as received. The same applies to the other two diols employed here, viz. dianhydro-D-glucitol or D-isosorbide (monomer **V**, Scheme 4) and bis(1,4-hydroxymethyl)benzene (monomer **VI**, Scheme 4). The absence of detectable impurities in these commercial products was however confirmed by FTIR and both ^{1}H and ^{13}C NMR spectroscopy.

2.2 Monomers for DA polymerisations

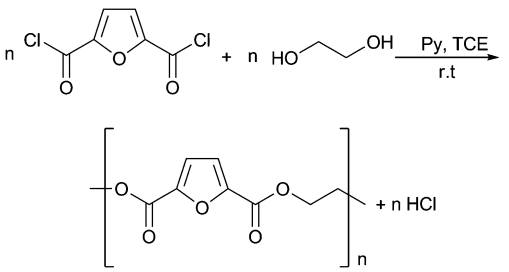
Both linear and branched polymers are discussed in this investigation, hence the preparation of monomers with two or more functionalities. The DA combination studied here is the most thoroughly examined couple in this type of polymer synthesis, viz. that involving the furan heterocycle as the dienic partner and the maleimide moiety as the complementary dienophiles.[3,4] The structures of the bisfuran monomers were chosen with the purpose of preparing flexible polymer chains, i.e., materials with relatively low Tg. Monomer **VII** (Scheme 5) was synthesised, purified and characterised following a previously reported procedure involving the esterification of adipoyl chloride with furfuryl alcohol in the presence of triethylamine.[6]

The preparation of monomer **VIII** (Scheme 5) called upon two steps, viz. the formation of the double Schiff base from furfural (20% molar excess) and 4,7,10-trioxa-1,13-tridecanediamine in absolute methanol for 5 h at room temperature, followed by the reduction of the C=N bonds with an excess of $NaBH_4$ for 2 h at room temperature. This solution was concentrated under vacuum, diluted with $CHCl_3$ and washed several times with water. The organic phase was dried and the solvents removed under vacuum leaving a viscous oil (80% overall yield): ν (FTIR-ATR)/cm^{-1} 3305 (NH), 3109 (furan C=C), 2912 (asCH_2), 2862 (sCH_2), 1346 (C–N), 1103 (C–O–C), 1010 (ring breathing), 914 + 740 (furan CH); δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.63 (1H, br s, N*H*), 1.78 (2H, quintet, $CH_2CH_2CH_2$), 2.70 (2H, t, CH_2NHCH_2), 3.50–3.64 (6H, m, 3 × OCH_2), 3.76 (2H, s, furan-CH_2NH), 6.16 (1H, d, furan H_3), 6.30 (1H, dd, furan H_4), 7.35 (1H, d, furan H_5); δ_C (75 MHz; $CDCl_3$, Me_4Si) 29.8 ($CH_2CH_2CH_2$), 46.2 (CH_2NHCH_2), 46.4 (furan-CH_2NH), 69.7, 70.1 and 70.5 (3 × OCH_2), 106.7 (furan *C3*), 110.0 (furan *C4*), 141.6 (furan *C5*), 154.0 (furan *C2*). An identical protocol was applied to the synthesis of trisfuran monomers **IX** and **X** (Scheme 5) from tris(2-aminoethyl)amine and Jeffamine T-403 (a commercial oligopropylene oxide primary triamine), respectively, both prepared in 90% overall yield. **IX**: ν (FTIR-ATR)/cm^{-1} 3105 (NH), 3113 (furan C=C), 2887 (asCH_2), 2819 (sCH_2), 1146 (C–N), 1008 (ring breathing), 916 + 728 (furan CH); δ_H (300 MHz; $CDCl_3$, Me_4Si) 2.10 (1H, br s, N*H*), 2.53 (2H, t, NCH_2CH_2), 2.63 (2H, t, NCH_2CH_2), 3.74 (2H, s, furan-CH_2NH), 6.14 (1H, d, furan H_3), 6.29 (1H, dd, furan H_4), 7.32 (1H, d, furan H_5); δ_C (75 MHz; $CDCl_3$, Me_4Si) 46.0 (NCH_2CH_2), 46.6 (furan-CH_2NH), 54.2 (NCH_2CH_2), 106.7 (furan *C3*), 110.0 (furan *C4*), 141.6 (furan *C5*), 153.8 (furan *C2*). **X**: ν (FTIR-ATR)/cm^{-1} 3113 (furan C=C), 2966 (asCH_3), 2939 (asCH_2), 2867 (sCH_2), 1146 (C–N), 1100 (C–O–C), 1010 (ring breathing), 917 + 730 (furan CH); δ_H (300 MHz; $CDCl_3$, Me_4Si) 0.80–3.54 (core jeffamine protons), 3.82 (2H, s, furan-CH_2NH), 6.16 (1H, d, furan H_3), 6.28 (1H, dd, furan *H*), 7.34 (1H, d, furan H_5); δ_C (75 MHz; $CDCl_3$, Me_4Si) 10–80 (core jeffamine carbons), 44.1 (furan-CH_2NH), 106.9 (furan *C3*), 110.4 (furan *C4*), 141.9 (furan *C5*), 154.6 (furan *C2*).

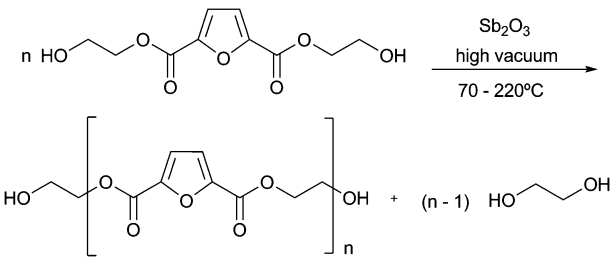


Scheme 5 Monomers used for the DA and retro-DA reactions.

The bismaleimide monomers **XI** and **XII** (Scheme 5) were prepared from the corresponding 1,6-diaminohexane and 4,7,10-trioxa-1,13-tridecanediamine in the classical two-step process involving the dehydration of the maleamic acid intermediates, as already reported.[6] The synthesis of the trifunctional maleimide monomer **XIII** (Scheme 5) employed the reaction of tris(2-aminoethyl)amine with the furan-maleic anhydride DA adduct (*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride), in stoichiometric conditions, carried out in absolute methanol at 56 °C for three days, which gave the corresponding trifunctional DA adduct as a yellowish solid precipitate. This intermediate was dissolved in toluene and submitted to the deprotective retro-DA reaction, by progressively liberating furan over 24 h of reflux. The ensuing yellowish solid, m.p. 170 °C, isolated by vacuum-evaporating the toluene, washing with hexane and drying (60% overall yield), gave a satisfactory structural characterisation, viz. ν (FTIR-ATR)/cm^{-1} 3098 (=CH), 2950 (asCH_2), 2858 (sCH_2), 1762 and 1687 (2 × C=O), 1121 (C–N); δ_H (300 MHz; $CDCl_3$, Me_4Si) 2.71 (2H, t, $(CO)_2NCH_2CH_2$), 3.52 (2H, t, $(CO)_2NCH_2CH_2$), 6.67 (2H, s, maleimide CH = CH); δ_C (75 MHz; $CDCl_3$, Me_4Si) 35.6 ($(CO)_2NCH_2CH_2$), 51.6 ($(CO)_2NCH_2CH_2$), 134.0 (maleimide CH = CH), 170.6 (C=O).



Scheme 6 **PEF** synthesis *via* the polycondensation of **I** with **IV**.



Scheme 7 **PEF** synthesis *via* the polytransesterification of monomer **II**.

3. Results and discussion

3.1 Polyesters

Furan polyesters have their own rather long history, first with scattered investigations,[7] often lacking in essential information, then with the thorough study conducted by Moore and Kelly in the late nineteen-seventies[8] and, more recently, with a series of studies dealing with the use of the difuran acid, chloride and esters shown in Scheme 3.[3] Several reasons prompted us to tackle anew this family of polymers, and more specifically those derived from **FDCA**, namely (i) the recent upsurge of major contributions to the preparation of **HMF** using highly efficient processes,[9] which places this compound in a novel industrial perspective by turning it into a viable commodity, consequently opening the way for the production of sizable quantities of **FDCA** at a reasonable price; (ii) the fact that among the numerous structures previously reported, that of the furan counterpart of the most important commercial polyester, poly(ethylene terephthalate) (**PET**), had not received any serious attention; (iii) the utilization of diol comonomers with specific features, including their renewable origin and/or their aptitude to give biodegradable polyesters.

The initial polycondensation processes selected for these syntheses called upon well-known mechanisms and procedures, albeit adapted to the novel context. In the specific instance of poly(ethylene 2,5-furandicarboxylate) (**PEF**), viz. the furan version of **PET**, the conventional system involving the dichloride **I** and ethylene glycol (monomer **IV**) reacting in 1,1,2,2-tetrachloroethane (TCE) at room temperature in the presence of pyridine (Scheme 6) gave the expected polyester (FTIR, NMR, see below), but with a rather low DPn of about 70.

In order to increase its molecular weight and apply a green process, we switched to a transesterification approach applied to monomer **II** (Scheme 4). After a series of runs aimed at finding the optimum polymerisation conditions, a satisfactory procedure was attained and adopted, as described here (Scheme 7). **II** was mixed with 1% of Sb_2O_3 in a round-bottom flask provided with a magnetic stirrer. The flask was connected to a high vacuum line through a liquid nitrogen trap and the temperature raised rapidly to 70 °C and then progressively to 220 °C under stirring in steps of ~10 °C, every time the condensation of the released ethylene glycol in the trap visibly stopped. This was accompanied by a continuous increase in viscosity, until the product turned into a solid mass, at which point the polymerisation was stopped by bringing the system back to room temperature. A brief account of this synthesis was previously published.[10]

In contrast to the **PEF** prepared from **I** + **IV** as described above, this material was insoluble in TCE and only dissolved in trifluoacetic acid (TFA) and in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), suggesting a higher DP and/or crystallinity. Its thorough characterisation first involved the verification of the expected polymer structure. The typical FTIR spectrum shown in Fig. 1 was essentially the same as that of its precursor **II**, except, as expected, for the absence of detectable OH bands at 3340 and 1080 cm^{-1}. The ^1H NMR spectrum of **PEF** in C_2F_6CDOD was entirely similar to that taken previously in TFA,[10] with two singlets with an integration ratio of 2, at 4.80 and 7.31 ppm, attributed respectively to the methylene and furan H3 + H4 protons. The ^{13}C NMR spectrum given in Fig. 2 is equally straightforward with signals at 64.5 ppm for the methylene carbons, 121.1 for the ring C3 and C4, 146.8 for the ring C2 and C5 and 160.9 for the carbonyl carbon.

In order to assess the DP of this polyester, two samples from different syntheses were each dissolved in TFA and treated with an excess of pentafluorobenzoyl chloride to esterify both terminal OH groups. After reprecipitation in methanol and thorough rinsing with it, the modified polymers were submitted to elemental analysis, which gave C 52.2 ± 0.3, H 3.4 ± 0.1, O 44.3 ± 0.3, F 0.38 ± 0.04, corresponding to a DPn of ~250, assuming complete end-group modification. This high molecular

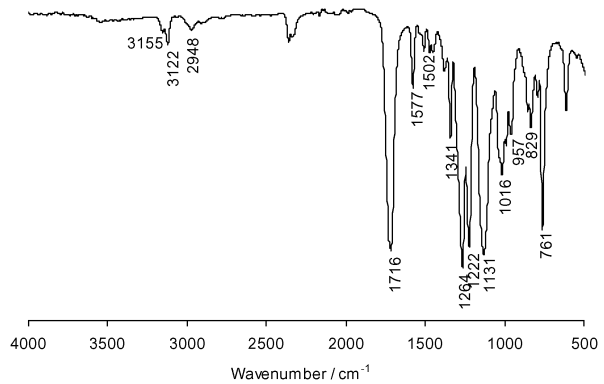


Fig. 1 FTIR spectrum of a sample of **PEF** prepared according to Scheme 7.

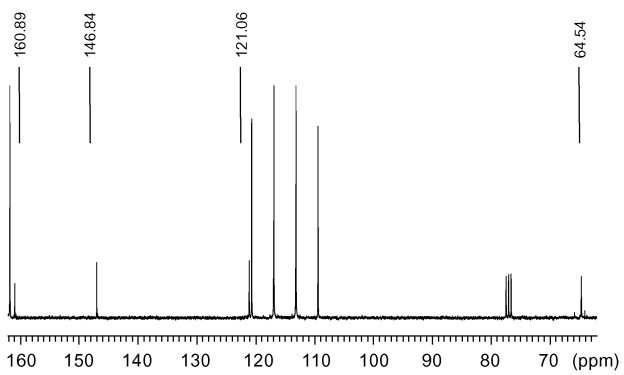


Fig. 2 ^{13}C NMR spectrum of a sample of **PEF** prepared according to Scheme 7 (solvent TFA with a drop of $CDCl_3$).

weight suggests that the transesterification conditions were quite adequate for monomer **II**.

These pristine **PEFs** displayed a high degree of crystallinity, as indicated by their X-ray diffraction pattern[10] and DSC thermograms (Fig. 3), the latter giving a melting temperature around 210 °C and a Tg, after quenching, close to 80 °C. A second scan, run after cooling **PEFs** slowly from the melt, only showed a melting endotherm at 212 °C, corroborating their high aptitude to crystallise. They were found to be thermally stable (Fig. 4) up to 300 °C, with a steep degradation feature around 400 °C.

Monomer **III** (Scheme 4) was submitted to the transesterification process described above for monomer **II** (Scheme 7)

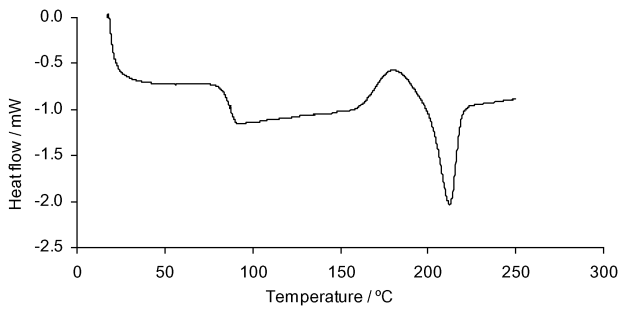


Fig. 3 DSC of **PEF** after melting the sample at 230 °C and quenching it in liquid nitrogen.

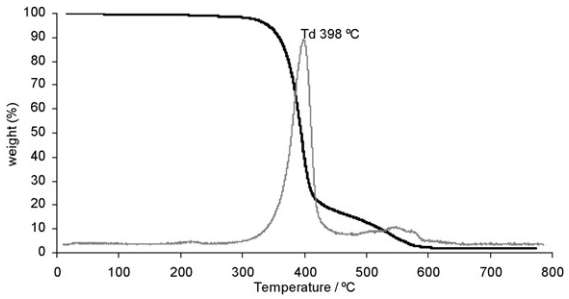
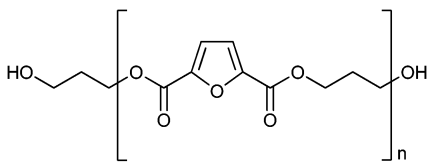


Fig. 4 Typical TGA of **PEF** in a nitrogen flow.

in order to prepare poly(propylene 2,5-furandicarboxylate) (**PPF**).



PPF

The only difference in behaviour was that, with this system, the vacuum removal of the less volatile condensation product was slower, but with 10^{-5} mmHg, all the released 1,3-propylene glycol was indeed trapped. As in the case of the minor spectroscopic differences between **II** and **III** discussed above, the FTIR and NMR spectra of **PPF** were very similar to those of **PEF**, except for the characteristic resonances associated with the extra middle CH_2 group. **PPF** had a melting temperature of 174 °C and a Tg of 65 °C, both lower than those of its **PEF** homologue, as expected, because of the higher macromolecular flexibility brought about by the additional methylene moiety in each polymer unit. Its thermal degradation in a nitrogen atmosphere started at ~300 °C with a drastic mass loss peaking at ~393 °C. The X-ray diffraction pattern of **PPF** gave peaks at $2\theta = 11.0$, 16.4, 22.5, and 27.8°. Its end-group derivatisation with pentafluorobenzoyl chloride in TFA and subsequent elemental analysis gave fluorine contents which again pointed to a DPn of about 250, thus confirming that the system chosen for the polymerisation of **II** applied equally well to **III**.

The use of non-volatile diols precludes the application of the process of transesterification adopted above for **PEF** and **PPF**. We reverted therefore to the conventional polycondensation process described above and illustrated in Scheme 6 to synthesize two additional furan polyesters based on **I** and diols **V** and **VI**, respectively.

The product of **I** + **V**, *i.e.* with both monomers from renewable resources, was isolated by precipitation in methanol (85% yield). The results of its characterisation were compared with those reported in a similar brief study.[11] Its FTIR, spectrum shown in Fig. 5 and not reported previously, suggested a relatively high DP because of the absence of any OH absorption around 3400 cm^{-1}. Both the ^1H and ^{13}C NMR spectra were in tune with previous data and confirmed the anticipated polyester structure **XIV**.

Its Tg was close to 180 °C (highly stiff monomer sequence) and its thermal degradation under nitrogen started at ~350 °C with complete mass loss at 450 °C.

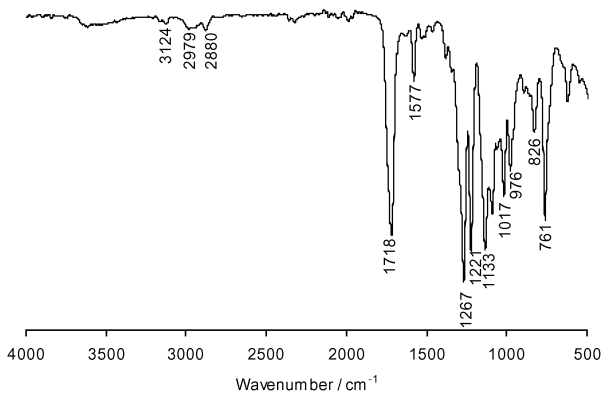
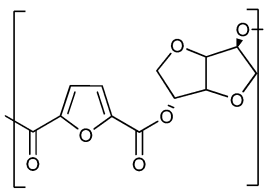
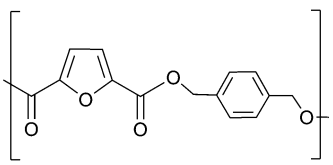


Fig. 5 FTIR spectrum of polyester **XIV**.



XIV

The polyester prepared with **I** + **VI** in 75% yield after precipitation in methanol, gave clean-cut spectra which corroborated the expected structure **XV**. Fig. 6 shows its FTIR spectrum which again lacked any absorption in the OH stretching region. The ^{1}H NMR resonances of its solution in C_3F_6DOD appeared at 5.38 ppm for the methylene protons, 7.30 for the furan H3 and H4, and 7.43 for the aromatic counterparts, with the correct integration ratio of 2:1:2. The ^{13}C NMR spectrum in the same solvent gave peaks (δ, ppm) at 66.4 (CH_2), 120.4 (furan C3 and C4), 128.9 (unsubstituted aromatic carbons), 135.7 (*para*-substituted aromatic carbons), 147.1 (furan C2 and C5) and 160.7 (*C*=O). The Tg of this novel polyester was close to 90 °C and its degradation under nitrogen began at ~300 °C. The melting temperature of its crystalline domains was 185 °C. Hence, the presence of both furan and aromatic rings, separated by carboxymethylene moieties, gave rise to thermal transitions in the same temperature range as with **PET** and **PEF**, and a reasonable aptitude to crystallisation.



XV

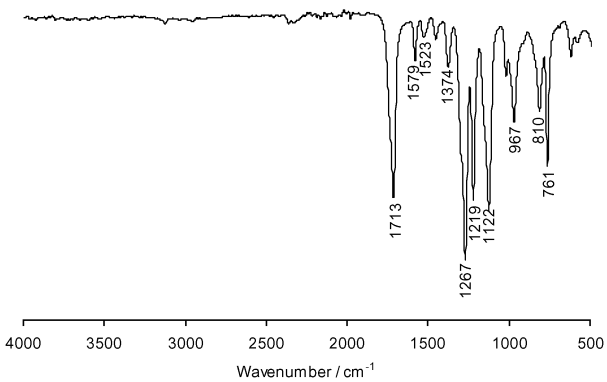


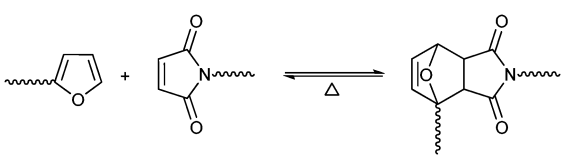
Fig. 6 FTIR spectrum of polymer **XV**.

3.2 Diels–Alder polymers

Scheme 8 illustrates the essence of the mechanism involved in the present DA and retro-DA reactions, which occur at every step of the polymer growth or of its unzipping, whether linear or branching. The emphasis here is on the role of the temperatures chosen to shift drastically the equilibrium from predominant adduct formation (polymerisation), viz. 65 °C, to the predominant reversion to its precursors (depolymerisation), viz. 110 °C. Systems of this kind are excellent examples of reversible click chemistry applied to macromolecular synthesis. The stereochemical aspects related to the relative abundance of the *exo* and *endo* forms of the adducts are not relevant in this specific context, since both play the same role as chain links between monomer units.

The formation of linear macromolecules from the step-growth mechanism associated with the successive DA reactions involving the bisfuran monomers **VII** and **VIII** and their complementary bismaleimides **XI** and **XII** was achieved by letting equimolar solutions of each pair (at concentrations varying from 0.1 to 2 M) in TCE or its deuterated counterpart evolve at 65 °C while stirring under nitrogen. The progress of the reactions was followed by UV and ^{1}H NMR spectroscopy and more qualitatively by the increase in the viscosity of the medium, particularly when high initial monomer concentrations were selected. The first technique provided quantitative information on yield/time evolution by monitoring the progressive decrease of the maleimide peak at 293 nm, associated with the corresponding loss of conjugation between the two carbonyl groups and the C=C unsaturation separating them, which accompanies the formation of the DA adduct. Fig. 7 shows one of these sets of spectra, recorded for the DA polymerisation of **VII** + **XII**. The presence of an isosbestic point, common to all these experiments, clearly suggests that the polymerisation was not marred by side reactions.

The second-order rate constants obtained with all these polymerisations were in good agreement with those obtained previously from reactions of monofunctional model compounds (furfuryl acetate and *N*-methyl maleimide) in the same conditions.[6] This observation is not surprising, since in both types of systems, the DA reaction involves the same diene and dienophile structures, *i.e.* a furan heterocycle substituted at C2 with a methylene group and a maleimide ring *N*-substituted by the



Scheme 8 The DA equilibrium between growing species bearing respectively furan and maleimide end groups.

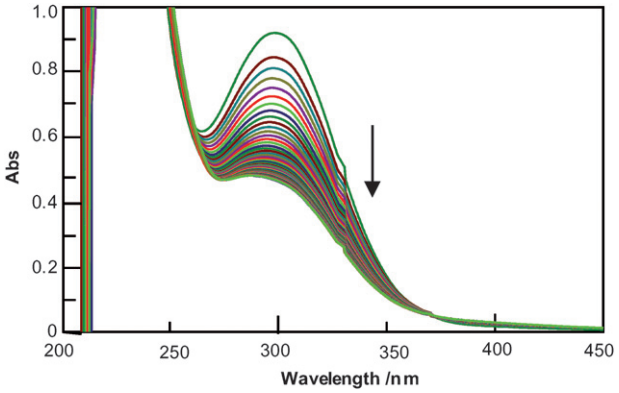


Fig. 7 Progressive decrease in the absorbance of the maleimide peak following the progress of the DA polymerisation of **VII** (0.2 M) with **XII** (0.2 M) in TCE at 65 °C. Spectra were taken every hour during 60 h with an optical path of 0.1 mm.

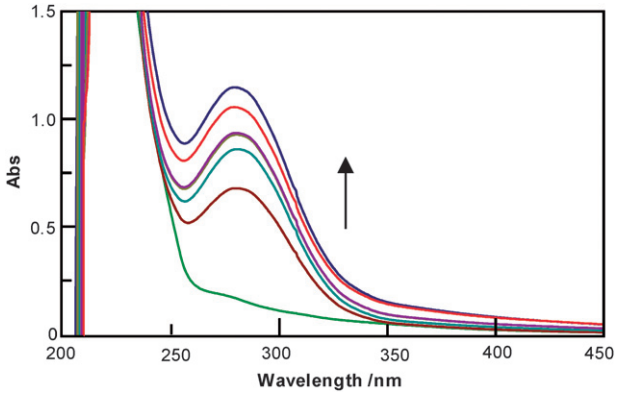


Fig. 9 Progressive increase in absorbance following the advancement of the retro-DA depolymerisation of polymer **VII** + **XI** in TCE at 110 °C. The regeneration of the monomers took about 24 h.

same moiety. In other words, the reactivity of both DA partners did not depend detectably on the nature of their substituents beyond their first carbon atom.

The use of ^{1}H NMR spectroscopy to follow these polymerisations revealed all the details of the progressive increase in the signals associated with the adduct protons and the corresponding decrease of those attributed to the unreacted furan and maleimide cycles. Fig. 8 shows a typical spectrum related to the near-completion of the DA polycondensation of **VII** with **XI**.

The retro-DA depolymerisation of these materials was followed at 110 °C by the same techniques. Fig. 9 shows a representative example of the UV spectroscopy observations.

For some systems, several polymerisation/depolymerisation cycles were applied reproducibly. In one instance, the polymer prepared from **VII** and **XI** was dissolved in toluene and submitted to the retro-DA reaction at reflux for 24 h, after which an excess of 2,5-dimethylfuran (DMFu) was added to the solution while cooling the system to 65 °C and leaving it for a further 24 h. After the vacuum removal of toluene and the unreacted DMFu, the residue was analysed by ^{1}H and ^{13}C NMR spectroscopy and shown to be an equimolar mixture of monomer **VII** and the bis-adduct of **XI** with DMFu. This result indicated that the polymer had indeed reverted to its monomers during the treatment in refluxing toluene (110 °C), but that the excess of

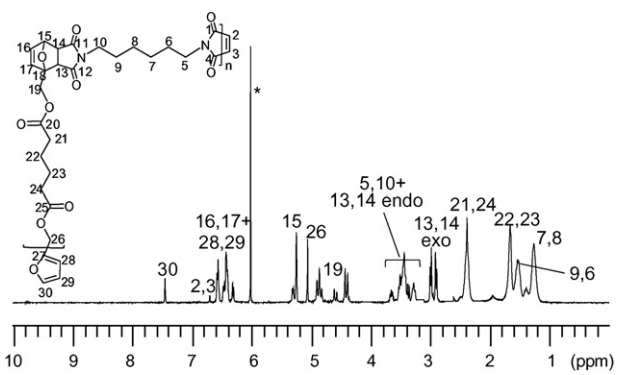


Fig. 8 ^{1}H-NMR spectrum of the DA linear polymer **VII** + **XI** prepared in TCE-d_2 (*) at 65 °C.

DMFu had trapped the bismaleimide **XI** during the phase at 65 °C by forming the corresponding bisadduct, thus inhibiting its DA repolymerisation with **VII**. A similar strategy had already been applied to avoid the return to a network structure after the decrosslinking of DA-based gels.[12,13]

The investigation of the non-linear DA polycondensations between each bisfuran and the trismaleimide **XIII**, or between each bismaleimide and each trisfuran, was carried out in the same experimental conditions and using the same spectroscopic tools. As expected, the use of complementary moiety stoichiometry produced a gel with every combination, whereas as the relative amount of trifunctional monomer was decreased, the reactions stopped short of crosslinking, *i.e.* gave soluble highly branched polymers. As a typical example of the behaviour of these systems, the reaction of bisfuran **VII** with the trismaleimide **XIII** was conducted at 65 °C in TCE or TCE-d_2 with three [maleimide]/[furan] molar ratios *r*, viz. 1.0, 0.75 and 0.50, which, according to Flory-Stockmayer equation,

$$Pc = \frac{1}{[r + r\rho'(m'-2)]^{1/2}}$$

(in the present context, m = 3 for monomer **XIII** and ρ = 1 because there is no other maleimide-type monomer in the system) are associated with critical conversions Pc for network formation of 50, 71 and 100%, respectively, if intermolecular cyclisations are neglected. Again, these reactions were followed by both UV (monomer concentrations of ~0.1M) and ^{1}H NMR spectroscopy (monomer concentrations of ~1M) and obviously here the increase in viscosity was much more pronounced than in the corresponding linear DA polymerisations discussed above. The reactions conducted with r = 1.0 with monomer concentrations close to 1 M, produced the most rapid thickening and gelled within a few days. Their counterparts with r = 0.75 displayed similar features, albeit in a slower mode and the reduction of r to 0.50 only showed a slow progressive increase in viscosity without attaining a gel point, which is in tune with the fact that crosslinking would only be reached at 100% conversion in the absence of ring formation.

The evolution of the UV spectra with reaction time mimicked the features exemplified in Fig. 7, again accompanied by the regular occurrence of an isosbestic point. Fig. 10 shows the

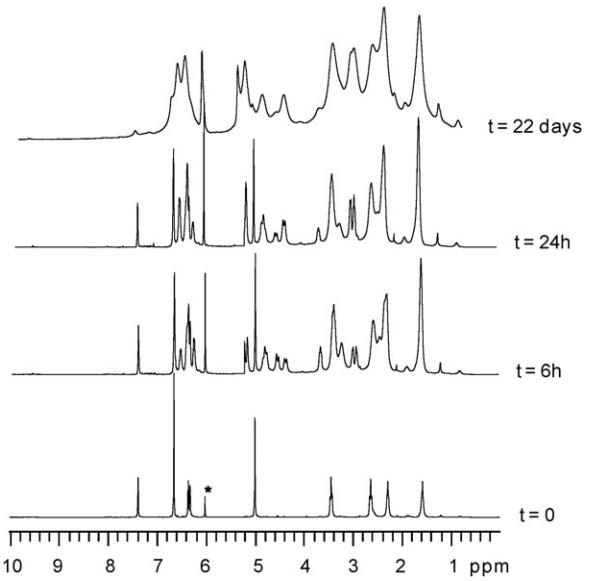
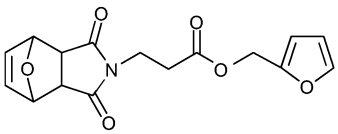


Fig. 10 ^{1}H NMR spectra of the evolution of the system **VII** + **XIII**, r = 1 at 65 °C (* TCE-d_2).

changes with time in the ^{1}H NMR spectra of the system **VII** + **XIII** under stoichiometric conditions (r = 1.0). Apart from the specific decrease and growth related to the peaks associated with furan and maleimide protons and to those of the ensuing adducts, respectively, which were already examined and attributed in the study of the linear DA polymerisations (Fig. 8), the other relevant phenomenon was the considerable widening of all resonances reflecting the dramatic increase in molecular weight. Indeed, the last spectrum was taken well after the formation of the network, *i.e.* a mixture of crosslinked (gel) and branched (sol) macromolecules.

These gelled products were then heated at 110 °C and the spectra taken at regular intervals revealed the occurrence of the retro-DA depolymerisation (visually observed by the progressive dissolution of the gel fraction), giving a pattern that simulated the reverse sequence of that shown in Fig. 10. The repetition of this cycle produced the same quantitative phenomenologies. In one instance, the system depolymerised at 110 °C was allowed to cool to 65 °C, after adding an excess of the DMFu DA trap, and left to react at that temperature for 24 h before vacuum removing the unreacted DMFu and part of the TCE-d_2. The spectrum of the ensuing solution displayed the resonances of monomer **VII** together with those of the **XIII**-DMFu trisadduct, confirming the efficiency of the retro-DA depolymerisation in the regeneration of the starting monomers. The other non-linear polymerisations displayed the same general features.

An additional challenge in the application of the DA reaction to furan polymers is the synthesis and polycondensation of monomers bearing both reactive moieties in their structures, *i.e.* AB, ABn and AnB molecules. The only study of one such system involving an AB monomer[14] was rather ill conceived in that the furan and maleimide cycles were too close to each other and this seemed to affect their smooth DA multi-coupling. We have now synthesised several more viable AB structures, like monomer **XVI**, using amino acids as precursors. The reaction of their amino function with the furan DA adduct of maleic anhydride generated a protected maleimide moiety at one end of the molecule and the esterification of their carboxylic function with furfuryl alcohol introduced a furan heterocycle at the other end.[15]



XVI

These compounds are stable towards polymerisation until their adduct end-group is deprotected through the retro-DA reaction above about 100 °C, which releases furan and generates the maleimide moiety. Hence the actual AB monomer is prepared in situ and its polymerisation can now be initiated at temperatures at which the equilibrium in Scheme 8 is predominantly shifted to the right. The interest here lies in the fact that AB monomers provide the ideal stoichiometric situation for linear polycondensations. These polymerisations have been studied, together with the corresponding retro-DA monomer regeneration, and shown to occur without any side reaction over several cycles.[15]

4. Conclusion

The ongoing research discussed here on a couple of topics related to furan polymers will hopefully give a glimpse into the relevance of a much broader field in terms of building a viable alternative approach to macromolecular materials based on renewable resources. While the furan polyesters represent promising examples of how to replace counterparts derived from fossil sources, the exploitation of the Diels–Alder reaction opens original possibilities in terms of polymers with novel properties and applications. Both topics are being pursued in order to widen the range of materials, through, among other structures, novel furan polyesters and copolyesters and hyperbranched DA polymers.

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